Ring Contraction of 1,2-Digermacyclohexa-3,5-dienes Initiated by Electron Transfer Reactions with TCNE

Kunio Mochida,* Hiromi Shimizu, and Masato Nanjo
Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Tokyo 171-8588

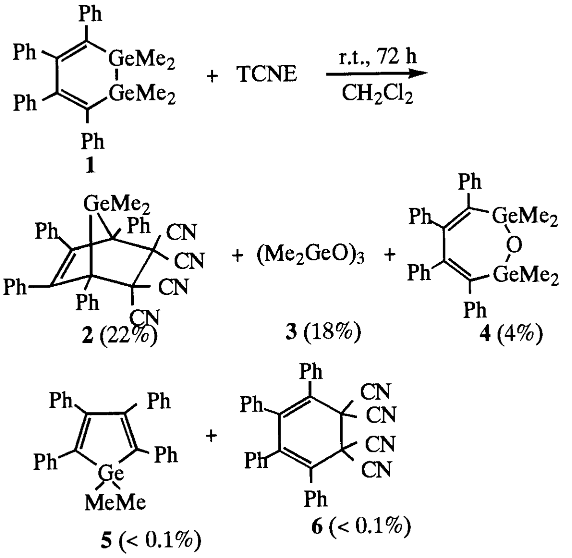
(Received July 25, 2000; CL-000706)

The thermal reaction of 1,2-digermacyclohexa-3,5-dienes with tetracyanoethylene (TCNE) gave 1-germacyclopenta-2,4-diene as a germylene extrusion compound through a charge-transfer complex. The 1-germacyclopenta-2,4-diene was trapped with TCNE to give 5,5,6,6-tetracyano-7-germanorbornene.

Group 14 element-group 14 element σ bonds with rather low ionization potential are excellent electron donors. As electron-rich species, these group 14 element catenates are subject to cleavage by various organic electrophiles as well as transition metal complexes through a charge-transfer (CT) complex.[1] While the CT interactions between silicon–silicon σ bonds and common electron acceptors such as tetracyanoethylene (TCNE) have been amply investigated,[2–7] there have been few reports on those of germanium–germanium σ bonds.[3] In a previous paper, we reported the CT spectra of permethylated oligogermanes ($Me(Me_2Ge)_nMe$)–TCNE, followed by insertion of TCNE into the germanium–germanium bonds of $Me(Me_2Ge)_nMe$.[8] During the course of our study on an electron-transfer reaction of germanium–germanium σ bonds, we found a ring-contraction reaction of 1,2-digermacyclohexa-3,5-dienes with TCNE under mild thermal conditions. The ring contracted compound, 1-germacyclopenta-2,4-diene, as a germylene extrusion compound through a CT complex was trapped with TCNE to give a stable 5,5,6,6-tetracyano-7-germanorbornene.

A solution of 1,1,2,2-tetramethyl-1,2-digerma-3,4,5,6-tetraphenylcyclohexa-3,5-diene[9] (**1**) (0.01 mmol) and TCNE (0.01 mmol) in dichloromethane was placed in a Pyrex tube under argon and sealed. The color of the solution changed from yellow to green. The reaction mixture was allowed to stand at room temperature for 75 h to give 5,5,6,6-tetracyano-7,7-dimethyl-1,2,3,4-tetraphenyl-7-germanorbornene (**2**, 22%), 2,2,4,4,6,6-hexamethyl-1,3,5-trioxa-2,4,6-trigermacyclohexane (**3**, 18%), and 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1,3-digermacyclohepta-4,6-diene (**4**, 4%). Trace amounts of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**5**, < 0.1%) and 5,5,6,6-tetracyano-1,2,3,4-tetraphenylcyclohexa-1,3-diene (**6**, < 0.1%) were also detected with GC–MS. The rest of **1** (51%) remained unreacted. Products **1**–**6** were characterized by NMR and GC–MS spectra in comparison with those of authentic samples.[9–11] In spite of all efforts to minimize moisture and air, **3** and **4** were obtained in substantial amounts.

The effect of the ratio of **1**/TCNE on the yield of **2** in the present CT reaction under the similar reaction conditions was examined. Increase in the concentration of TCNE relative to **1** did not influence the yields of **2**.



The reaction of 1-germacyclopenta-2,4-diene **5** with TCNE at room temperature for 15 min gave a new 7-germanorbornene **2** quantitatively. The 7-germanorbornene **2** was identified by spectroscopic analysis.[12] The molecular structure of **2**[13] was characterized by single-crystal X-ray crystallography (Figure 1). The 7-germanorbornene **2** shown in Figure 1 has distorted geometry, with bond lengths of C(1) or C(1)*–Ge(7) (2.0269 Å) and bond angle of C(1)–Ge(7)–C(1)* (112.26 °).

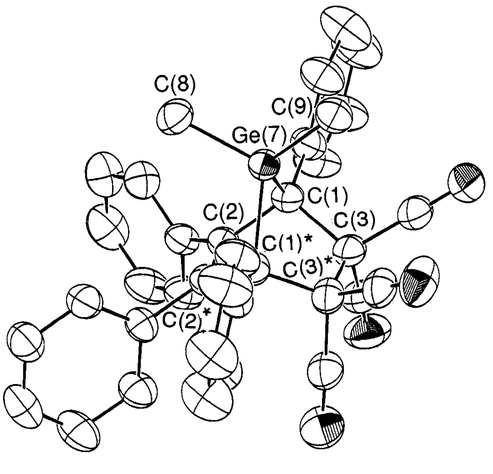
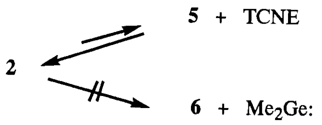


Figure 1. The crystal structure of **2**. Selected bond lengths (Å) and angles (°): Ge(7)-C(9) 1.952(2), Ge(7)-C(8) 1.939(2), Ge(7)-C(1) or C(1)* 2.0269(15), C(1)-C(2) 1.5314 (19), C(1)-C(3) 1.593 (2), C(2)-C(2)* 1.355(3), C(3)-C(3)* 1.629 (3), C(9)-Ge(7)-C(8) 111.02(11), C(9)-Ge(7)-C(1) 119.55(7), C(1)-Ge(7)-C(1)* 112.26(7), C(9)-Ge(7)-C(1)* 112.26 (7), C(2)-C(1)-C(3) 105.22(12), C(2)-C(1)-Ge(7) 97.19(9), C(3)-C(1)-Ge(7) 101.94(10), C(1)-C(2)-C(2)* 113.38(8), C(1)-C(3)-C(3)* 107.19(8).

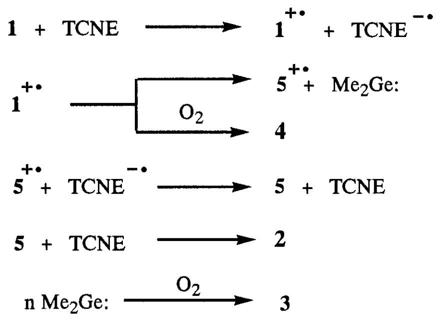
The bond lengths of C(1) or C(1)*–Ge(7) are longer than those of Ge–Me (1.939 and 1.952 Å) in **2**. The new 7-germanorbornene **2** is stable at room temperature for at least 72 h, but very slowly decomposes at above 70 °C. Unexpectedly, ^{1}H-NMR showed that thermolysis of **2** at 70 °C for 4 h gave 1-germacyclopenta-2,4-diene **5** in 7% yield. The presence of **5** suggests the formation of TCNE at the same time. The rest of **2** (92%) remained unreacted. No formation of products derived from germylene and **6** was detected by ^{1}H-NMR. The result is in marked contrast to that in the reaction of 2,3-benzo-7-germanorbornenes at 70 °C for 3 h.[14]



The color of the solution of **1** and TCNE in dichloromethane strongly suggests the CT interaction between **1** and TCNE. The formation of a CT complex is evidenced by the ESR spectrum of the TCNE radical anion (g = 2.0031, a_N = 1.56 G) at room temperature.[3]

From these results, we propose the following scheme as one possible reaction pathway.

At first, electron transfer from 1,2-digermacyclohexa-3,5-diene **1** to TCNE generates the geminate radical ions composed of the radical cation of **1** ($\mathbf{1}^{+\cdot}$) and the radical anion of TCNE (TCNE^{-}**)**. The radical cation of 1-germacyclopenta-2,4-diene **5** ($\mathbf{5}^{+\cdot}$) and dimethylgermylene (Me_2Ge:). The formation mechanism of **4** and **5** with extrusion of Me_2Ge: generated from $\mathbf{1}^{+\cdot}$ has been reported.[12]



Scheme 1.

Some parts of $\mathbf{1}^{+\bullet}$ react with oxygen to give 1,3-digerma-2-oxacyclohepta-4,6-diene **4**. The radical cation $\mathbf{5}^{+\bullet}$ is reduced by $\mathrm{TCNE}^{-\bullet}$ to afford **5** and TCNE. The compound **5** thus formed reacts with TCNE to give 7-germanorbornene **2**. The germylene reacts with oxygen to afford **3**.

We thank Dr. Masanobu Wakasa of the Institute for Physical and Chemical Research (Riken) for measuring ESR spectra of the TCNE radical anion. The authors also thank Mitsubishi Material Co., Ltd., for providing us tetrachlorogermane.

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12 **2**: mp. 149–150 °C; ^{1}H NMR (δ, $CDCl_3$) 1.17 (s, 3 H), 1.36 (s, 3 H), 6.79–7.31 (m, 20 H); MS (*m/z*) 460 (M^+ – TCNE).
13 Crystal data for **2**: $C_{36}H_{26}GeN_4$; FW = 587.20; crystal size 0.4 × 0.3 × 0.2 mm; monoclinic, space group $P2_{1/m}$, Z = 2; a = 8.8680 Å, b = 20.1090 Å, c = 8.9420 Å, β = 93.013°; V = 1480.59 Å^3, D = 1.317 g/cm^3; Goodness of fit = 1.040, R = 0.0382, R_w = 0.1139, 3494 reflections measured.
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